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PHOTOCHEMICAL CHLORINATION OF METHANE.

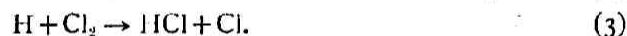
By MIKIO TAMURA.

The photochemical chlorination of methane proceeds by a chain mechanism. Coehn and Cordes¹⁾ found a quantum yield of 10^4 . This reaction bears a close resemblance to the hydrogen-chlorine reaction^{2),3)}, and therefore the reaction mechanism is assumed to follow either of the two alternative schemes:

I.



II.



Simple considerations make the former seem more probable. This point will be referred to later.

Unlike the hydrogen-chlorine reaction, the methane-chlorine reaction is complex on account of the variety of the chlorides produced. As the reaction proceeds, methylene chloride, chloroform and carbon tetrachloride are formed besides methyl chloride. This renders it difficult to measure the velocity of the reaction between chlorine and methane alone. Therefore it is desirable to measure the reaction rate at an early stage of the reaction, where only methyl chloride is a little produced and the formation of other chlorides can be neglected. This is the very condition satisfied when we use the method of thermal analysis of reaction velocity which originated with Prof. S. Horiba^{4),5),6)}. This method enables us to measure the rate

1) Coehn and Cordes, *Z. physik. Chem.*, B, 9, 1 (1930).

2) Jones and Bates, *J. Am. Chem. Soc.*, 56, 2282 (1934).

3) Pease and Walz, *J. Am. Chem. Soc.*, 53, 3728 (1931).

4) S. Horiba and T. Ichikawa, *This Journal*, 1, 145 (1927); "Sexagint" (a collection of papers dedicated to Prof. Y. Osaka) 73 (1927). T. Ichikawa, *This Journal*, 4, 1 (1930); *Z. physik. Chem.*, B, 10, 299 (1930).

5) M. Tamura, *This Journal*, 11, 1 (1937).

6) M. Tamura, *ibid.*, 7, 49 (1933).

in the course of the first few seconds of the reaction, in which methyl chloride is the main product and the formation of more highly chlorinated products is negligible. In fact, the partial pressure of the methyl chloride formed throughout the whole course of our experiments has been calculated to be less than 1 mm. Hg. As the initial pressure of methane is 179 mm. Hg and the reaction velocity of chlorination of methyl chloride, if present in the same amount as methane, is of the same order of magnitude as that of chlorination of methane^{11,12}, the effect of successive substitution on the measurement is negligible in the present experiments.

The present author has so far studied the photochemical chlorination of hydrogen⁹, the photochemical union of carbon monoxide and chlorine⁶, and the chlorine-sensitized oxidation of carbon monoxide⁷ by this method and measured the mean lives of reaction chains, concentrations of chain carriers and collision yields of some partial reactions and so on. Similar measurements have now been made about the photochemical chlorination of methane and the reaction mechanism discussed.

Experimental Method.

Here will be given only an outline of the experimental method. For further information, refer to the previous reports^{4, 5, 6}. The pressure increase Δp of a gas mixture due to the heat of reaction was recorded on a photographic film, mica membrane and optical lever being used properly⁸. From this record the reaction velocity $\frac{dx}{dt}$ can be calculated by the following equation,

$$K \frac{dx}{dt} = \frac{d(\Delta p)}{dt} + k(\Delta p), \quad (1)$$

where K and k are constants, the values of which can be easily obtained. K is proportional to the heat of reaction⁹ and k refers to the cooling of the gas mixture.

We can thus calculate the reaction velocity at any time during the period of illumination and after shutting off light. See, for example, Figs. 1 and 2.

7) M. Tamura, *ibid.*, 9, 150 (1935).

8) The reaction vessel was a cylindrical Pyrex-glass tube of about 3.7 cm. in diameter and about 13.6 cm. in length, both bases of which were made of quartz plates. The vessel had a side tube with a thin mica membrane.

9) According to Thomsen, *Z. physik. Chem.*, A, 52, 343 (1905) and E. Schj nberg, *ibid.*, A, 172, 197 (1935), the heat of combustion of CH_3Cl is about 177 kcal. Using this value and other thermal data, we obtain



According to Bichowsky and Rossini's "Thermochemistry of Chemical Substances" (1936), the reaction heat is 23.8 kcal. But in the present paper we use 23.3 kcal. for the calculation.

Preparation of Reactants.

Chlorine was prepared by electrolysis of a solution of potassium chloride acidified with hydrochloric acid. The gas was purified by washing with water and then with sulphuric acid, both in darkened vessels, and was passed through a tube filled with glass balls and heated at 350°C., and then was collected with solid carbon dioxide. This chlorine was then subjected to repeated fractional distillations in vacuum.

Methane was prepared from aluminium carbide and purified by the procedure due to R. Schenck¹⁰. Just before the experiment, the methane thus obtained was subjected to repeated fractional distillation in vacuum.

In all procedures much care was taken as to the exclusion of oxygen.

Experiments.

The reaction vessel was washed several times with chlorine, and the grease used was that treated with chlorine and heated in vacuum. The initial partial pressures of gases were read by a mercury manometer, a spring manometer of Pyrex glass being used as the zero point instrument to avoid the direct contact of mercury with chlorine.

In general, the sensitivity of the gas mixture to light varied during the period of illumination, probably due to the destruction of impurities. This change of sensitivity became very small when methane was very carefully purified. The methane used in the present experiments was of such a high purity as no noticeable change of sensitivity was observed when illuminated for 3 minutes. Throughout the whole course of the present experiments, the total time of illumination was only about 30 seconds. The reproducibility was, therefore, satisfactory. Notwithstanding our careful purification, a small amount of impurities must have been present in the gas mixture. But it must be emphasized here that the results of calculation given later on are entirely uninfluenced by the presence of the small amount of impurities.

The reaction vessel, light source, filters and others were the same as used in the experiments previously carried out by the author^{5),6),7)}. The light source was a 1000 C.P. Pointolite lamp, operated from a battery supply. The light was passed through a 78 mm. layer of a solution ($\frac{\text{CuSO}_4 + 2160 \text{ NH}_3}{180}$ Molar) and neutral tint filters of various transparency¹¹. The light beam was rendered approximately

10) R. Schenck, *Z. anorg. Chem.*, **164**, 145 (1927).

11) The absorption of chlorine taken into consideration, 4400 Å can be regarded as the mean wave length of the light and used for the calculation of quantum yield.

parallel and slightly smaller in diameter than that of the cylindrical reaction vessel. The initial partial pressure of methane was 179 mm. Hg and that of chlorine 111 mm. Hg. The initial pressure of methyl chloride was 0.0 mm. Hg and the final pressure less than 1 mm. Hg. The experiments were carried out at room temperature (19°C.).

A) Change of the Reaction Velocity during Exposure. Effect of Light Intensity and Quantum Yield.

The reaction velocities during the period of illumination calculated by equation (1) using experimental records are given in Fig. 1. In this figure J 's represent light intensities in arbitrary unit. The numbers under the curves indicate the experimental numbers. As is seen from the figure, upon illumination the reaction velocity increases rapidly to reach a constant value, which is the velocity in

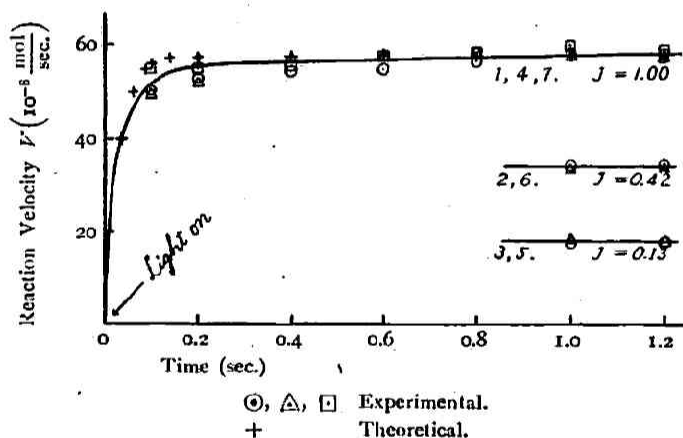


Fig. 1. Change of Reaction Velocity during Exposure.

photostationary state. In this figure, for the reactions by weaker lights, only the velocities in photostationary state are given. From the above experimental data, we notice that the reaction velocity in the stationary state is proportional to 0.6-th power of light intensity, namely,

$$\frac{dx}{dt} = kJ^{0.6} \quad (2)$$

As is seen in Table 1, k is constant enough to justify the above expression. The quantum yields were also measured¹⁰. The smaller the velocity in the photostationary state was, the larger the quantum yield was as shown in Table I and Fig. 3.

Table I.

(Cl₂)=111 mm. Hg, (CH₄)=179 mm. Hg. Temperature: 19°C.

Expt. No.	Light Intensity / in Arbitrary Unit.	Reaction Velocity in Photostationary State (10^{-8} mol/sec.)	k	Quantum Yield
1) 4) 7)	1.00	57.3	57	2700
2) 6)	0.42	34.0	57	3810
3) 5)	0.13	17.8	61	6430

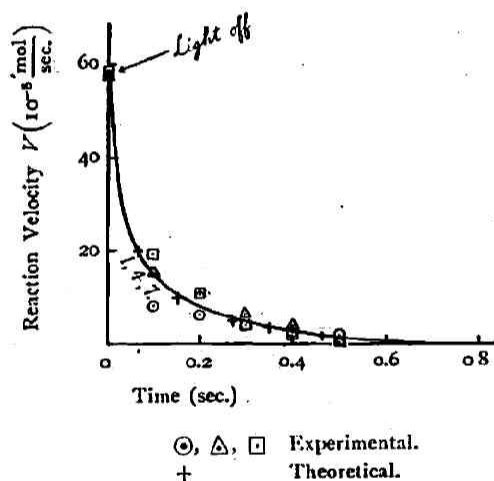
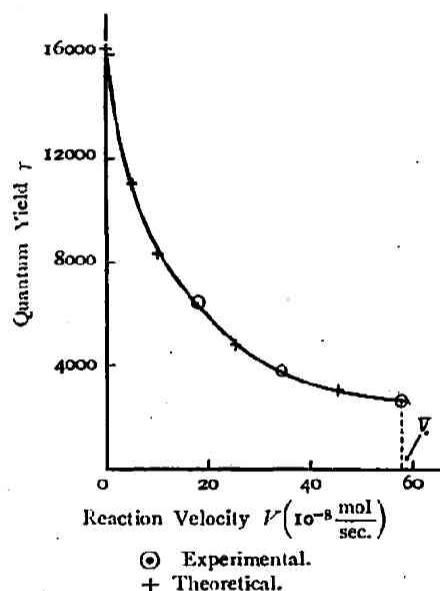


Fig. 2. Change of Reaction Velocity after Shutting off Light.

Fig. 3. The Relation between the Reaction Velocity in Photostationary State and the Quantum Yield (or $2 \times$ the Mean Length of Chain).

After shutting off light, the reaction velocity did not immediately vanish, but it ran as shown in Fig. 2. The curve indicates the change of the reaction velocity in Expts. No. 1, 4 and 7 after shutting off light.

Discussion.

A) Collision Yield of Partial Reaction, $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3.$

As will be explained later, the reaction mechanism which the present author prefers is neither I nor II given above. But temporarily we use the scheme I

for simplicity. This does not affect the results of calculation given below.

Now let the time taken for a chain link be τ sec., then one molecule of hydrogen chloride are formed by a chlorine atom in τ sec. The life of a chain is given by $T = \tau \nu$, ν being the chain length or the number of chain links in the chain.

Just as in the case of hydrogen-chlorine reaction⁶⁾, we can easily evaluate T and ν and hence τ from our experimental results. The mean life of chain, T_m , after shutting off light is obtained from the velocity curve in Fig. 2. Let V_0 represent the reaction velocity at the moment of shutting off light, then T_m is given by

$$T_m = \frac{1}{V_0} \int_0^\infty V dt. \quad (3)$$

Thus, from Fig. 2. we have $T_m = 0.962 \times 10^{-1}$ sec. As the chain length is one half of the quantum yield, the mean chain length ν_m , which corresponds to T_m , is obtained from Fig. 3. in the following way. Since the experimental results show that the velocity is proportional to 0.6-th power of the light intensity, it is possible to conclude that the reaction chains are terminated principally by the combination of chain carriers between themselves rather than by such an inhibitor as oxygen. The chain becomes, therefore, longer, as the concentration of chain carriers becomes smaller or the reaction velocity becomes smaller, for the reaction velocity is proportional to the concentration of chain carriers. ν_m is, therefore, obtained from Fig. 3. by the following relation:

$$\nu_m = \frac{1}{2V_0} \int_0^{V_0} (\text{quantum yield}) dV. \quad (4)$$

Thus we get $\nu_m = 2800$. Hence τ is calculated to be 3.44×10^{-6} sec. τ is the time taken by a chain link, but the partial reaction (3) in I may be considered to be faster than the partial reaction (2) and the latter can be reasonably considered to take τ sec. τ depends, of course, upon the partial pressures of component gases and temperature, and can be considered as reciprocally proportional to the concentration of methane.

Now let us evaluate the collision yield of the reaction (2). The number of collisions of a chlorine atom with methane molecules in one second is given by

$$Z = 2 \sqrt{\frac{d_{Cl} + d_{CH_4}}{2}} \sqrt{\frac{M_{Cl} + M_{CH_4}}{M_{Cl} M_{CH_4}}} \cdot RT \cdot N_{CH_4}, \quad (5)$$

where d is the atomic or molecular diameter, M the atomic or molecular weight

12) Loeb, "Kinetic Theory of Gas" p. 527 (1927).

and N_{CH_4} , the number of methane molecules in 1 cm³.

Assuming that the chlorine atom is spherical and has the same density as that of chlorine molecules, we have $d_{\text{Cl}} = 2.6 \times 10^{-8}$ cm.¹²⁾ When the pressure of methane¹³⁾ is 1 atm. and the temperature 19°C., Z is 0.52×10^{10} . The collision yield of the partial reaction (2) is, therefore,

$$\frac{1}{0.52 \times 10^{10} \times \frac{179}{760} \times 3.44 \times 10^{-5}} = 2.4 \times 10^{-5} \quad (10)$$

Let E represent the activation energy of reaction (2) and p the steric factor, then

$$2.4 \times 10^{-5} = pe^{-\frac{E}{RT}} \quad (6)$$

Since p is equal to or less than unity, from equation (6) $E \leq 6.2$ kcal.

The reaction mechanism II given above contains a partial reaction, $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3\text{Cl} + \text{H}$. But this reaction is endothermic by about 21 kcal¹⁵⁾ and obviously incompetent as the partial reaction of a rapid chain reaction at room temperature. Moreover, according to our results the heat of activation of the rate determining partial reaction must be at most about 6.2 kcal, so the above reaction cannot be considered as a partial reaction. Thus the unsuitableness of the reaction mechanism II is evident.

B) Concentration of Chain Carriers. Mechanism of Chain Breaking.

We can estimate the concentration of chain carriers in the following way. Let n_0 represent the number of chlorine atoms produced by light in one c.c. in one second and T_{st} , the mean life of chain in photostationary state, then the product $n_0 T_{\text{st}}$ represents the number of chain carriers in 1 c.c. in photostationary state. T_{st} is given by $\frac{1}{2}\tau\gamma$, γ being the quantum yield. Thus in our experiments 1, 4 and 7, where $n_0 = 14.6 \times 10^{11}$, $\tau = 3.44 \times 10^{-5}$ sec. and $\gamma = 2700$, $n_0 T_{\text{st}}$ is 6.8×10^{10} . In other words the partial pressure of chain carriers is 1.9×10^{-6} mm. Hg. Now it is reasonable to assume that this partial pressure gives that of Cl (or possibly the

13) The diameter of methane molecule was assumed to be 3.14×10^{-8} cm.

14) This value is of the same order of magnitude as the collision yield of the reaction, $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$, obtained by the present author, the latter being 1.4×10^{-5} . (See foot-note 5).

15) $\text{CH}_4 + \text{Cl}_2 = \text{CH}_3\text{Cl} + \text{HCl} + 23$ kcal.

$\text{Cl} + \text{Cl} = \text{Cl}_2 + 57$ kcal.

$\text{HCl} = \text{H} + \text{Cl} - 101$ kcal.

$\text{CH}_4 + \text{Cl} = \text{CH}_3\text{Cl} + \text{H} - 21$ kcal.

sum of partial pressures of Cl and Cl_3 as will be explained later), for in the reaction mechanism I the partial reaction (3) will be fast in comparison with the reaction (2), and hence the mean life of the chlorine atom will be longer than that of CH_3 .

As the reaction velocity is proportional to a power of the intensity of light approaching to 0.5, it is concluded that the reaction chains are terminated principally by the combination of chain carriers between themselves, rather than by such an inhibitor as oxygen or by the wall of the vessel. Now first let us assume that 1.9×10^{-6} mm. Hg obtained above gives the partial pressure of chlorine atoms. Then we can easily calculate the number of ternary collisions, $\text{Cl} + \text{Cl} + \text{M}^{16)}$, which a chlorine atom suffers in one second in our experiments 1, 4 and 7. The result of calculation shows that the number of such ternary collisions is about 2.6×10^{-2} . It takes, therefore, about 40 seconds before a chlorine atom recombines in this manner. But as shown above, the mean life of chain in experiments 1, 4 and 7 is only $3.44 \times 10^{-5} \times 2700 \times \frac{1}{2} = 4.65 \times 10^{-2}$ sec., so that the chain breaking reaction cannot be $\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$. Similar result was also obtained in our experiment on the photochemical union of hydrogen and chlorine⁹⁾ and so we considered the possibility that the chain might be broken by the reaction $\text{Cl}_3 + \text{Cl}_3 \rightarrow 3\text{Cl}_2$. Rollefson and Eyring¹⁷⁾ put forward on quantum mechanical grounds the following mechanism for the recombination of chlorine atoms,



According to them, quasimolecule Cl_3 has a very long life as compared with the duration of an ordinary collision and hence ternary collision is unnecessary for the former reaction.

But recently Ritchie and Smith¹⁸⁾ measured the photoexpansion of chlorine under various conditions and their results agreed with the mechanism



Now let us examine whether this mechanism is available for our experiment or not. Let us assume that 1.9×10^{-6} mm. Hg given above represents the concentration of Cl_3 in the photostationary state in experiments 1, 4 and 7: then the time taken for a Cl_3 to disappear in the reaction $\text{Cl}_3 + \text{Cl}_3 \rightarrow 3\text{Cl}_2$ is calculated¹⁹⁾ to be

16) M represents a third body.

17) Rollefson and Eyring, *J. Am. Chem. Soc.*, 54, 170 (1932).

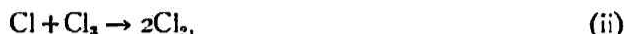
18) Ritchie and Smith, *J. Chem. Soc.*, 394 (1940).

19) Assuming that Cl_3 is spherical and has the same density as that of chlorine molecules, we get 3.8×10^{-8} cm. for the diameter of Cl_3 .

9.5×10^{-2} sec. by taking the collision yield as unity, and it agrees well with the mean life of chain in order of magnitude, the latter being 4.7×10^{-2} sec. as is given above. This indicates that the chain terminating reaction may be either



or



and that the concentration of Cl_3 must be either of the same order of magnitude as, or higher than, that of Cl . Craggs, Squire and Allmand²⁰⁾ introduced the following equilibrium to explain their experimental results on the photochemical union of hydrogen and chlorine.

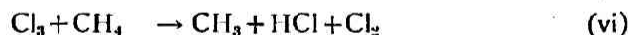


or



And according to them, reaction chains are ended by the disappearance of chlorine atoms and of Cl_3 radicals, both on the walls and, without ternary collisions, in the gas phase. As will be explained later on, in our experimental condition equilibrium (iii) or (iv) can be considered to exist. Taking the experimental results of Ritchie and Smith¹⁹⁾ into account, we prefer here (iv) to (iii). The equilibrium constant K_p , given by Craggs, Squire and Allmand²⁰⁾ is 0.0049 mm.^{-1} and that calculated from the data given by Rollefson and Eyring¹⁷⁾ 0.076 mm.^{-1} at 18°C . Hence in our experimental conditions, the concentration of Cl_3 is estimated to be of the same order of magnitude as that of Cl in agreement with our conclusion stated above.

Though Cl_3 is introduced, such reaction chains as



are to be neglected. According to Rollefson and Eyring¹⁷⁾ or to Craggs, Squire and Allmand²⁰⁾, the heat of activation of reaction (v) is 4.5—5 kcal. Hence the time taken for a Cl atom to make a Cl_3 radical in accordance with the reaction (v) is, in our conditions, about 10^{-3} sec.²¹⁾ and is very long as compared with the time taken for a chain link, 3.44×10^{-8} sec. According to Kimball and Eyring²²⁾ the collision yield of the reaction $\text{Cl}_3 + \text{H}_2 \rightarrow \text{Cl}_2 + \text{HCl} + \text{H}$ is 10^{-3} — 10^{-4} times the yield of Cl — H_2 collisions. There are some considerations, which are unfavorable

20) Craggs, Squire and Allmand, *J. Chem. Soc.*, 1878 (1937).

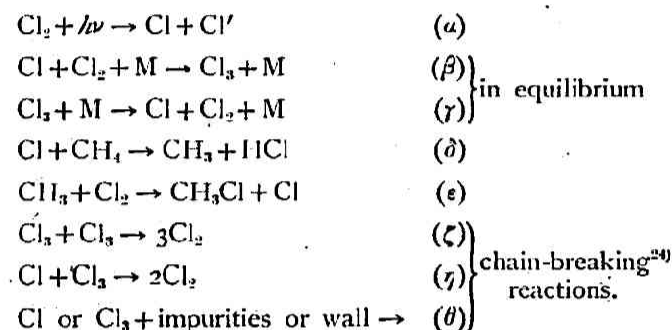
21) The third body M was assumed not to act catalytically and reduce the heat of activation.

22) Kimball and Eyring, *J. Am. Chem. Soc.*, 54, 3876 (1932).

to their view²³, but let us assume in our reaction which is similar to the hydrogen-chlorine reaction, that the yield of Cl_3-CH_4 collision is 10^{-3} times that of $\text{Cl}-\text{CH}_4$ collision. For these reasons we neglect reaction chains consisting of (v), (vi) and (vii).

In short, our experimental results accord with the following reaction mechanism.

III.



Under our experimental condition we can, as stated above, assume the concentration of Cl to be nearly equal to that of Cl_3 . If so, it is calculated that, in the photostationary state of the experiments 1, 4 and 7, 10^{13} — 10^{14} chlorine atoms and Cl_3 radicals per c.c. and per sec., are formed and lost by the reactions (β) and (γ)²⁵, and that 10^{12} chlorine atoms are produced by (α) and lost by (ζ) and (η) after conversion into Cl_3 radicals; 10^{12} Cl_3 radicals are lost by (ζ) while 10^{16} chlorine atoms react with methane in accordance with (δ) and are immediately regenerated by (ϵ). The disappearance of Cl and Cl_3 by (θ) is evidently negligible. Thus the conditions sufficient for the equilibrium between (β) and (γ) are nearly satisfied.

There is still a point to be referred to. As we assumed that the yield of Cl_3-CH_4 collision is 10^{-3} times as much as that of $\text{Cl}-\text{CH}_4$ collision, we are led to the result that 10^{12} Cl_3 radicals per c.c. and per sec., are lost by the reaction (vi) and the same amount of Cl atoms are immediately produced by (vii). This does not remarkably disturb the equilibrium. If the yield of Cl_3-CH_4 collision is larger than that assumed and hence the rate of conversion of Cl_3 radicals through

23) Rollefson, *J. Am. Chem. Soc.*, 56, 579 (1934).

24) The breaking of the chain by the disappearance of CH_3 may be neglected, owing to its low concentration. (θ) is of importance as compared with (ζ) and (η) only when the concentration of chain carriers is low.

25) The heat of activation of the reaction (γ) was assumed to be 7.5 kcal., according to Craggs, Squire and Allmand. See foot-note 20).

(vi) and (vii) into Cl is high, equilibrium will be disturbed and the ratio (Cl)/(Cl₂) will become large. But this is contrary to our conclusion that the concentration of Cl₂ radicals must be nearly equal to, or higher than, that of Cl atoms.

The above scheme III has been obtained under some assumptions, and it can not, of course, be considered to be perfect. But the results of the present experiments can be explained by it and not by I or II.

C) Equations Representing the Experimental Curves.

Theoretical considerations lead to the following equations representing the relation between the reaction velocity and time, and that between the quantum yield and the reaction velocity in photostationary state⁵⁾.

For the reaction velocity during the exposure we get

$$\frac{2.30}{Q} \log \frac{(A+2BV+Q)(A-Q)}{(A+2BV-Q)(A+Q)} = t, \quad (7)$$

where $Q = \sqrt{A^2 + 4NB}$. And the reaction velocity after shutting off light is given by

$$\frac{2.30}{A} \log \frac{V_0(A+BV)}{V(A+BV_0)} = t, \quad (8)$$

The relation between the quantum yield and the reaction velocity in photostationary state is expressed by

$$A + BV = \frac{1}{\tau\nu} = \frac{2}{\tau\gamma} = \frac{58200}{\gamma}. \quad (9)$$

In the above three equations, V represents the reaction velocity in the unit of $10^{-8} \frac{\text{mol}}{\text{sec.}}$, V_0 the reaction velocity in photostationary state, γ the quantum yield, t the time in sec., and A , B and N are constants whose values are 3.61, 0.34 and 1330 respectively. As to the details of these constants and the derivation of the above equations, refer to the report on the hydrogen-chlorine reaction⁵⁾. The point marked + in Figures 1, 2 and 3 are those obtained by the above equations. They are seen to fall near the experimental curves.

Summary.

1) The photochemical reaction between methane and chlorine has been investigated by the method of thermal analysis. Using this method we can avoid the confusion brought about by successive chlorination.

2) The mean life of reaction chains and the time taken for a chain link have been calculated. The results of the estimation of the concentration of chain carriers

indicate that the chain-terminating reaction is not of the ternary collision type, such as $\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$, but of binary collision type, such as $\text{Cl}_3 + \text{Cl}_2 \rightarrow 3\text{Cl}_2$ or $\text{Cl} + \text{Cl}_2 \rightarrow 2\text{Cl}_2$. The reaction mechanism is discussed and a plausible one given.

3) The collision yield of the reaction $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCl}$ is calculated to be 2.4×10^{-5} ; in other words, the heat of activation of this partial reaction is at most 6.2 kcal.

4) In the methane-chlorine reaction at room temperature, a mechanism containing a partial reaction, $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3\text{Cl} + \text{H}$, must be discarded.

In conclusion, the author wishes to express his hearty thanks to Professor S. Horiba for his kind guidance throughout this investigation.

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